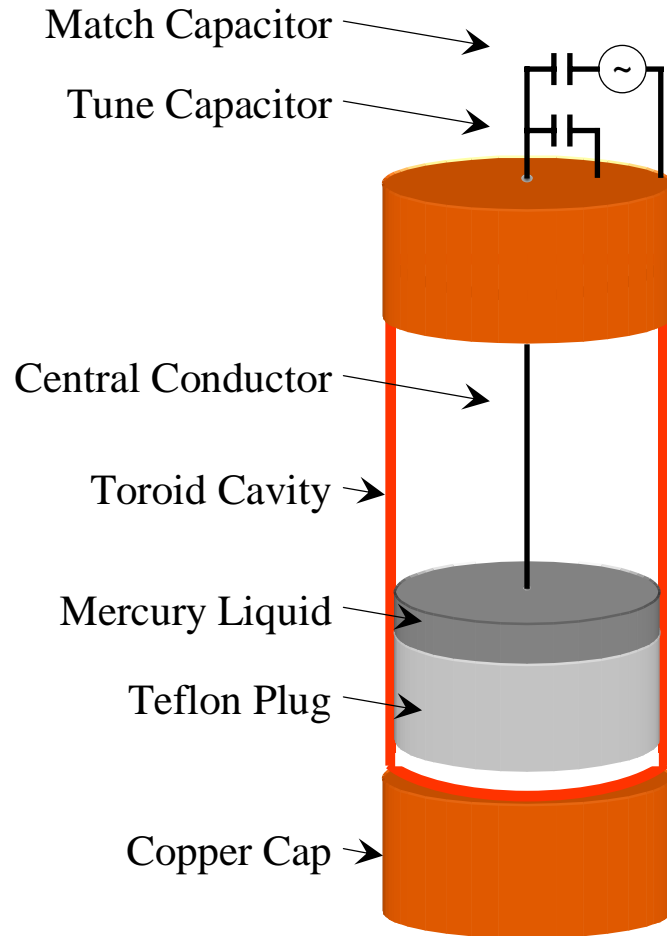


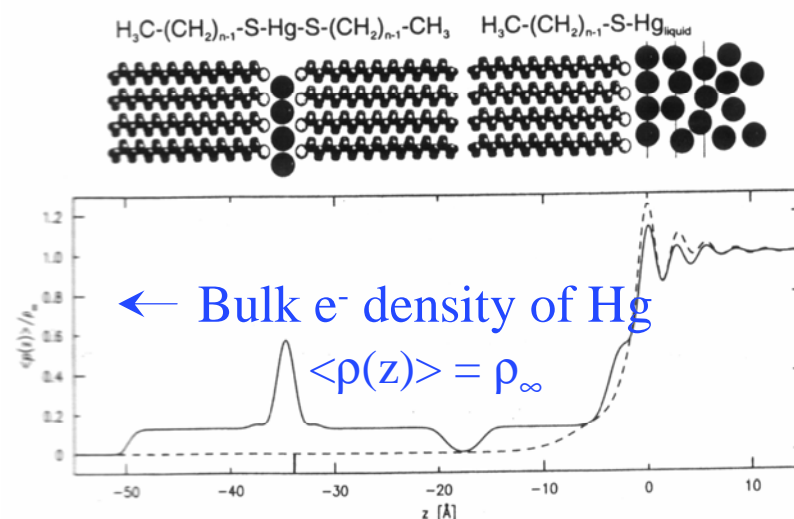
SAMs Imager



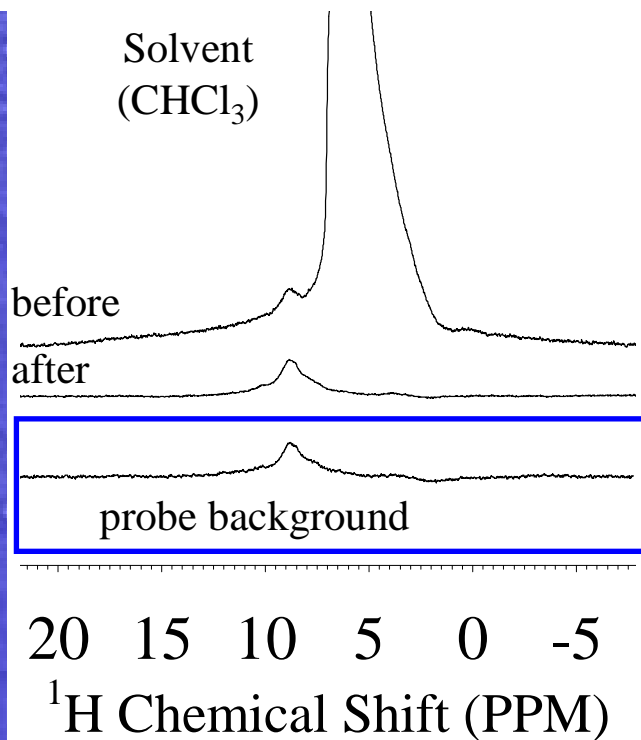
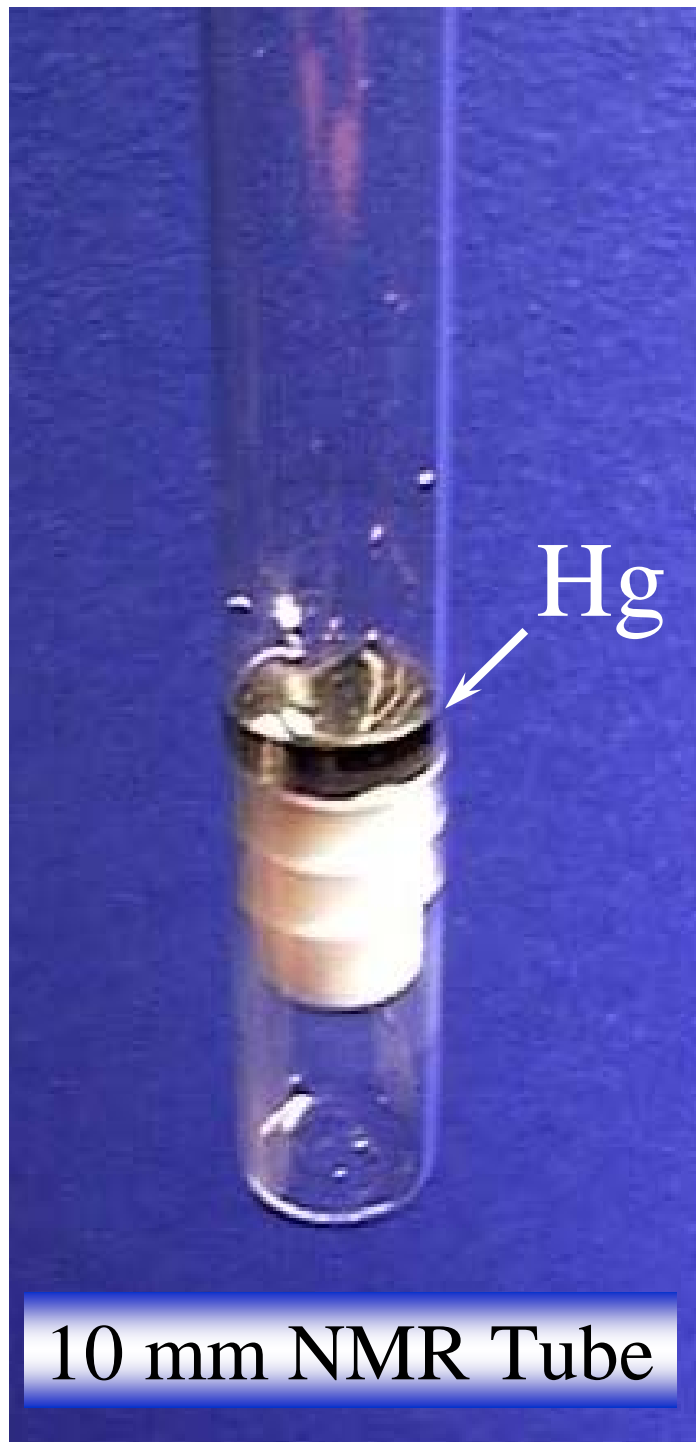
The novel NMR probe with enhanced sensitivity for investigations of self assembled monolayers (SAMs) used in our experiments was based on a toroid cavity detector, which we modified to incorporate a liquid metal surface. The mercury or gallium provides an atomically flat surface so that the SAM layers are well oriented in the B_0 field.

Molecular Self Assembly on Mercury

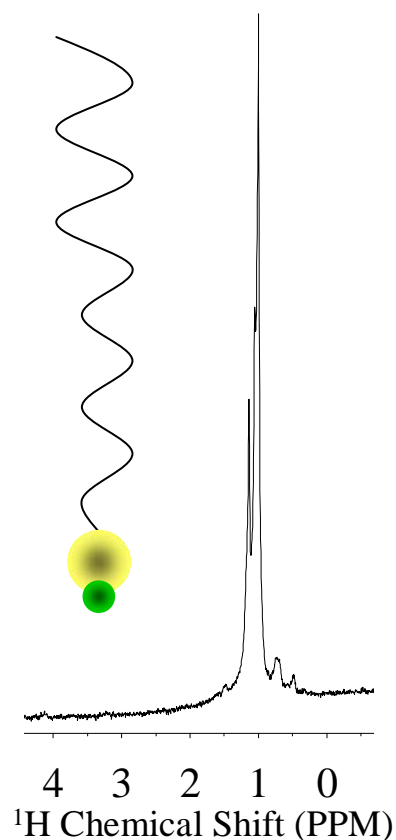
Pershan and coworkers determined normalized electron density profiles ($\langle \rho(z) \rangle / \rho_\infty$) from X-ray reflectivity measurements of dodecanethiol multilayers on mercury surfaces. The results were independent of the method used to prepare the thin films (depositions from solution, neat liquid, and vapor). The mercury provides: (a) an atomically flat surface that insures a uniform molecular order over a macroscopic area ($> 1 \text{ cm}^2$), and (b) electronic conductivity for RF currents necessary for NMR experiments.



*Magnussen, Ocko, Deutsch, Regan, Pershan,
Abernathy, Grübel, and Legrand
Nature
384, 250-252 (1996)*



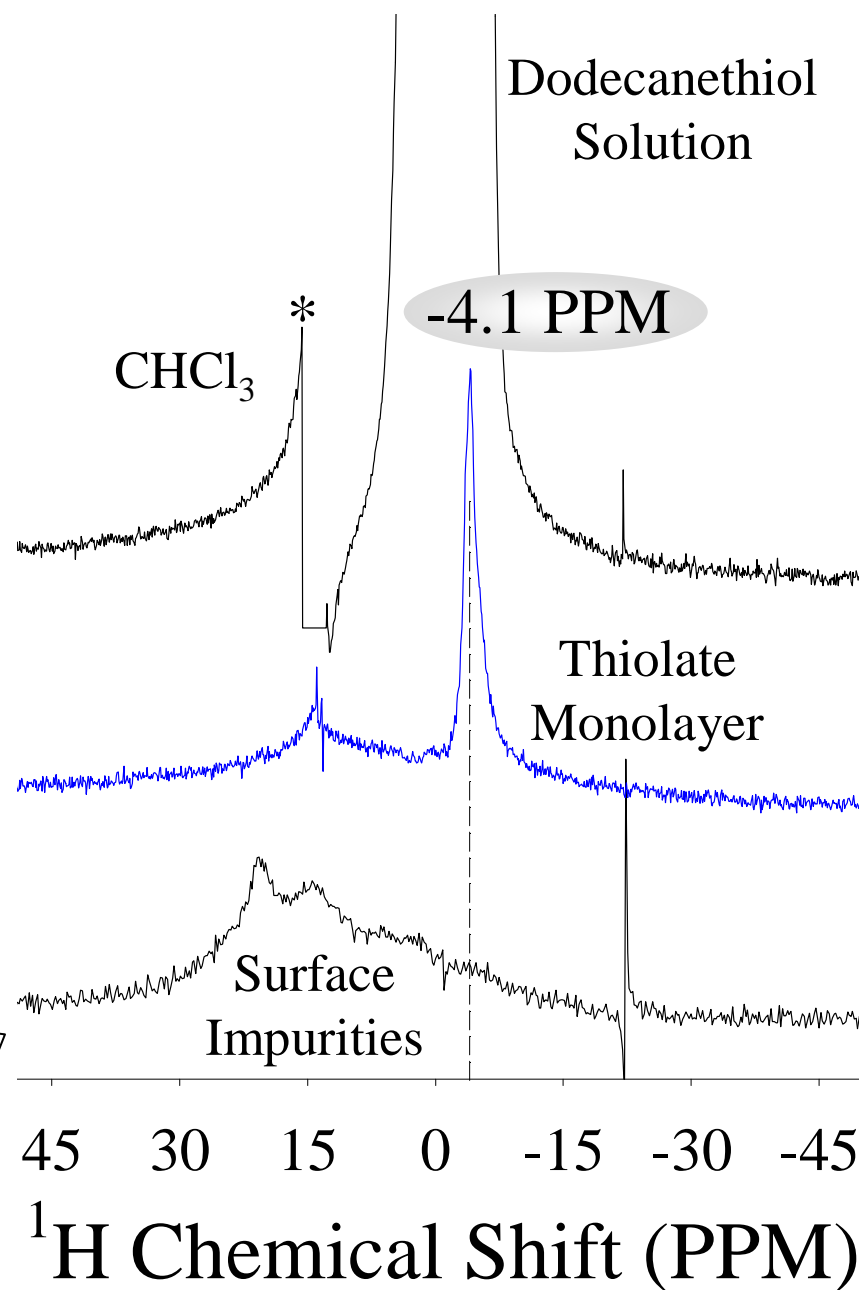
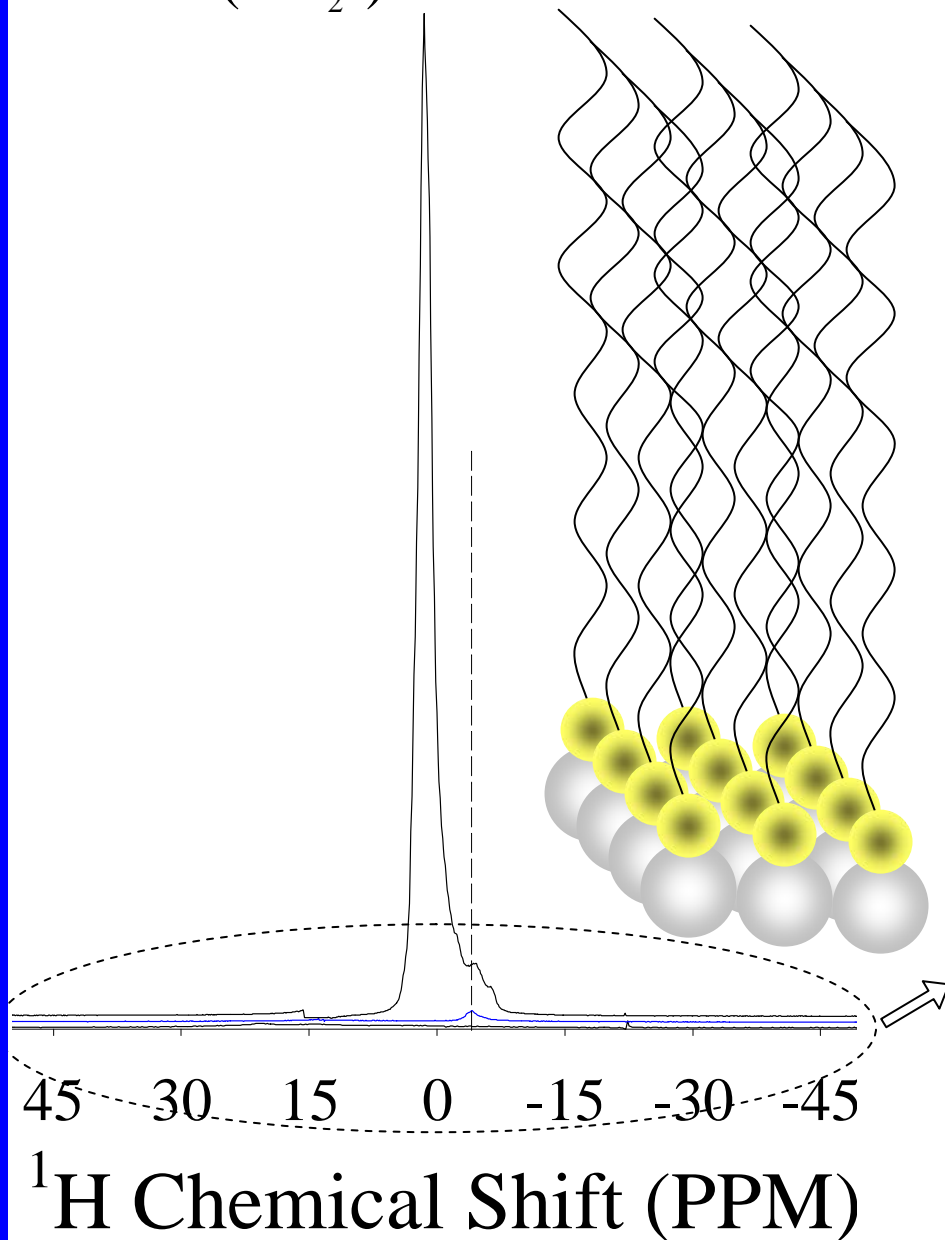
NMR spectrum of a solution of dodecanethiol above an Hg surface before and after evaporation of CHCl_3 . A 10-mm commercial probe was used. The Hg surface causes B_0 distortions and a long 90° pulse ($60 \mu\text{s}$). No evidence of a monolayer or thin film of alkane thiolate is seen by NMR.



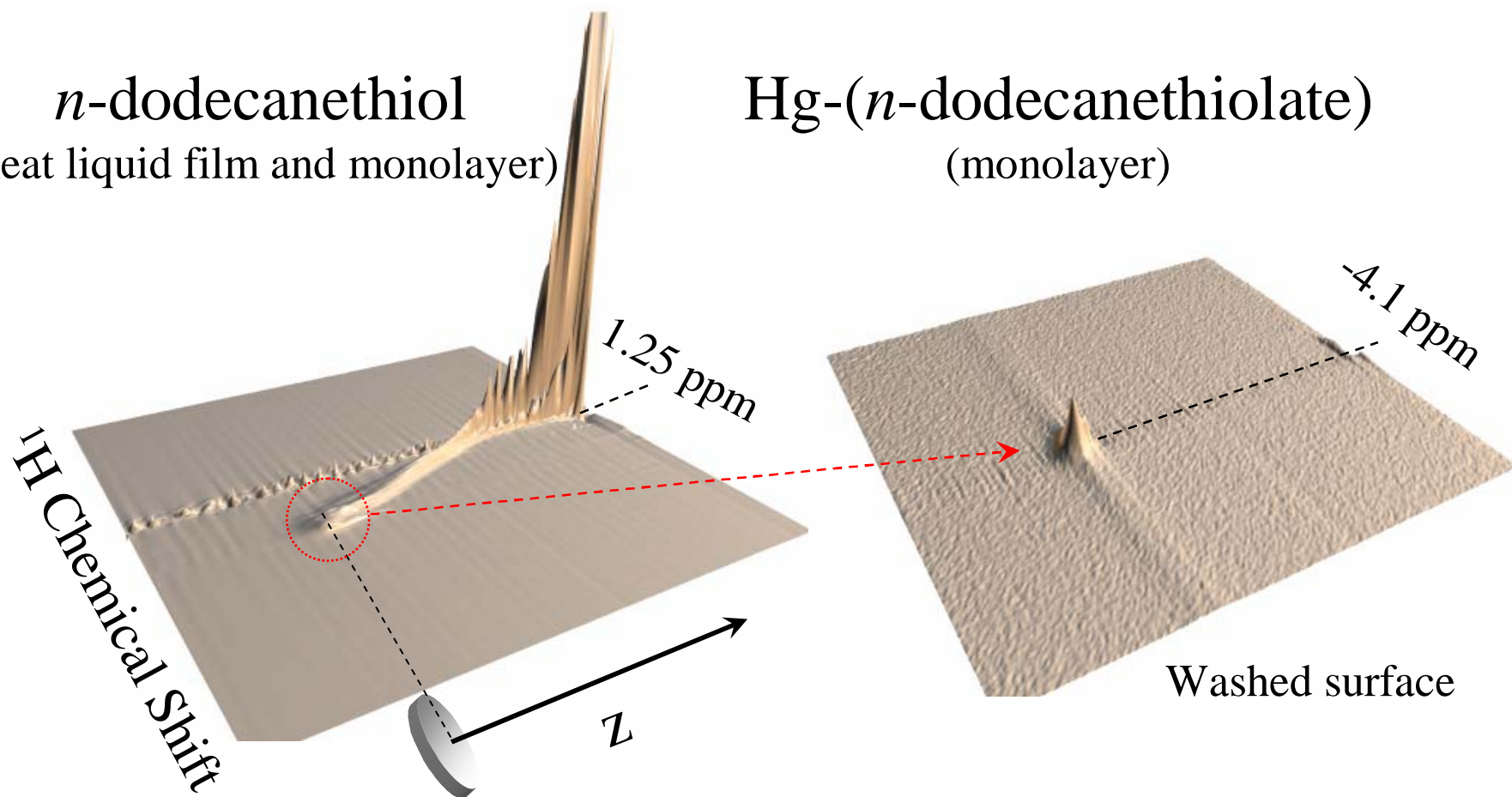
Dilute, high-resolution NMR spectrum of dodecanethiol in CHCl_3 (~ 1 monolayer / cm^3). The spectrum was collected in 30 min. and corresponds to ~ 2 monolayer equivalents.

The deposition of a solution of dodecanethiol on Hg

$\delta(-\text{CH}_2-) = 1.5 \text{ PPM}$

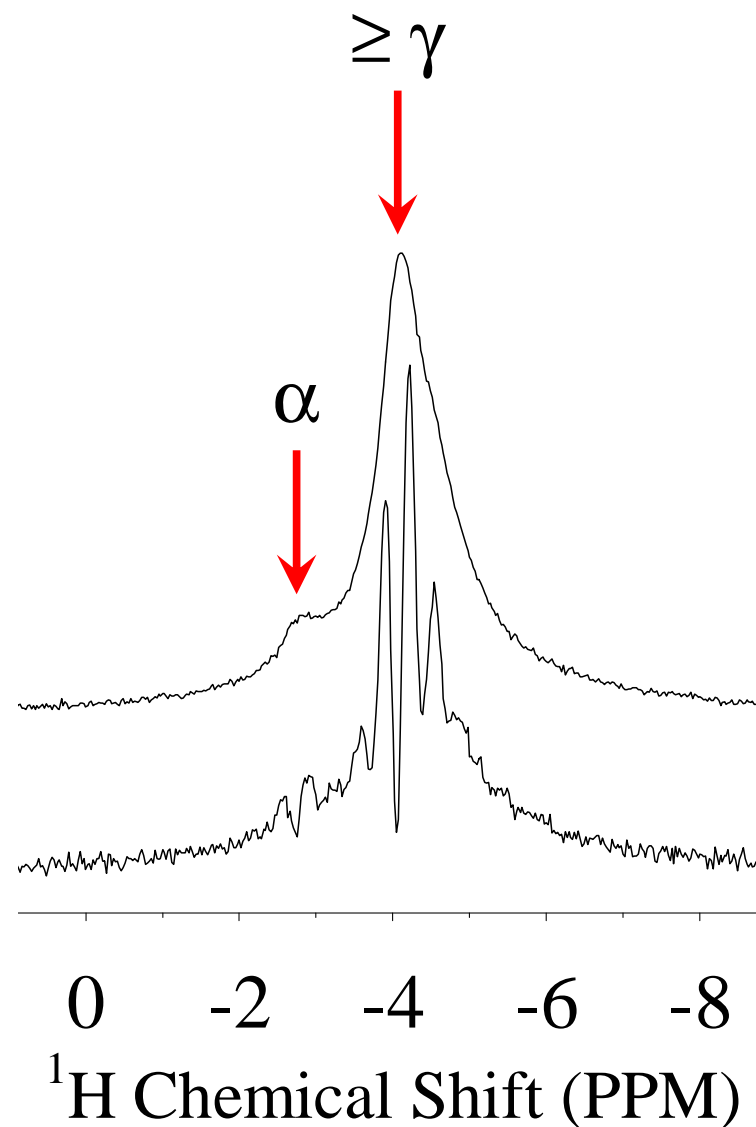
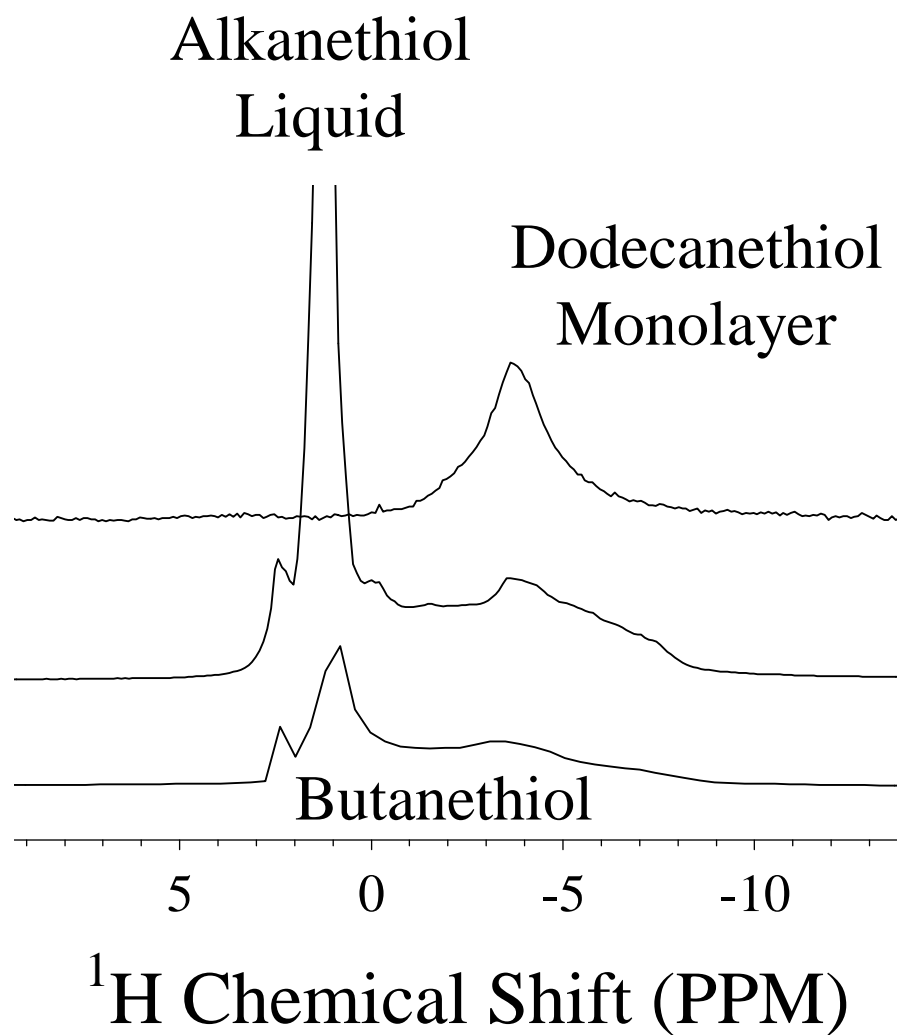


2-D Surface NMR

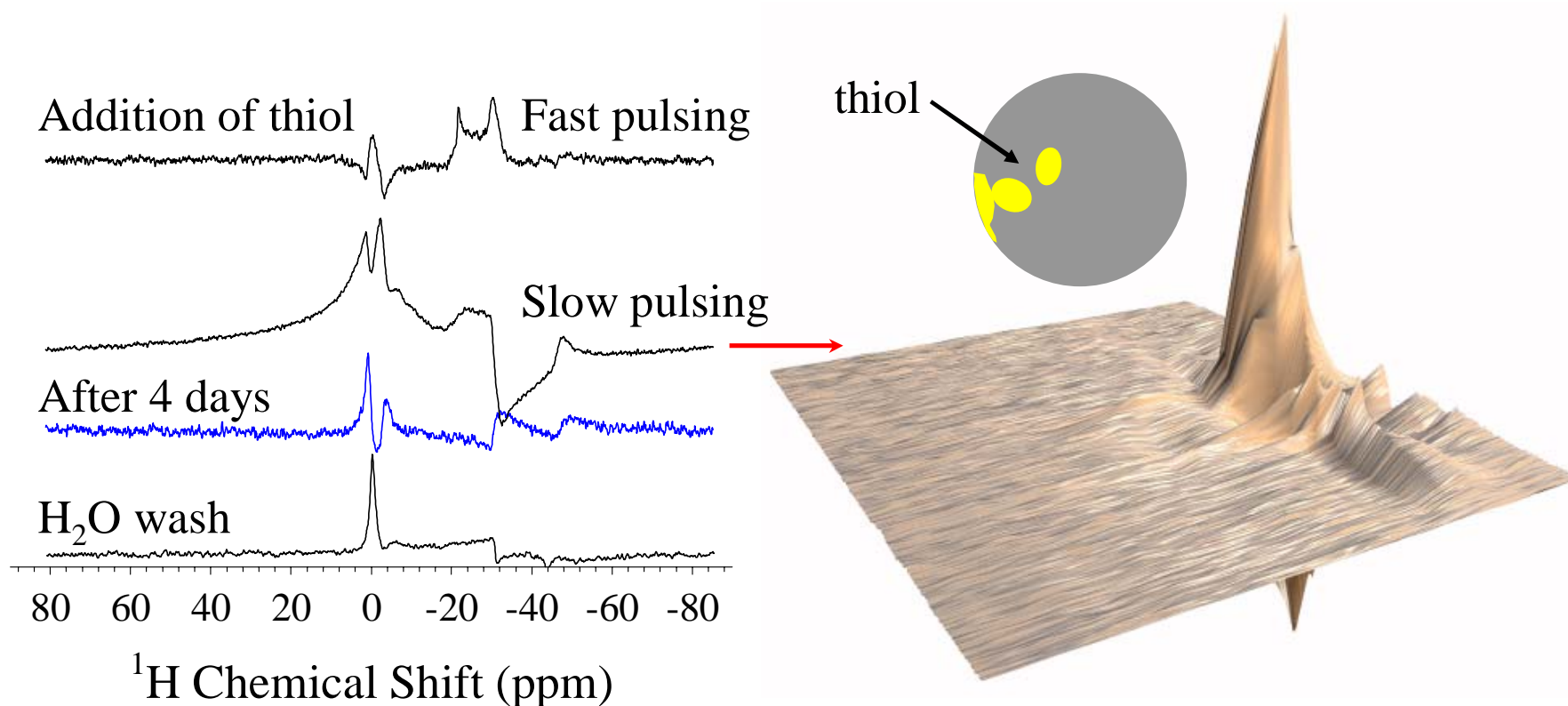


- Recorded using the rotating frame imaging method
- Continuous change in the chemical shift of $(\text{CH}_2)_n$ from the neat *n*-dodecanethiol liquid to the *n*-dodecanethiolate monolayer: Hg(II)bis(*n*-dodecanthiolate) bilayers
- Washed surface reveals monolayer

^1H NMR of Alkanethiol Monolayer on a Mercury Surface



Composite Film on Mercury



Less than one microliter of thiol was deposited in spots on the the mercury surface. The top three spectra taken of the composite surface show a new resonance. NMR images map chemical shift against nutation frequency (a measure of the magnitude of the radiofrequency magnetic field). The image compares the location of the new resonance to the original resonances recorded for the H₂O washed surface.

Key Points

- A limiting factor in previous NMR based SAM studies is the sensitivity of the probe. The probe employed in our experiments required 1-2 cm² of Hg surface to accomplish similar sensitivity
- The detector allowed us to observe dodecanethiol SAMs on Hg
- In temperature dependence studies it was determined that our probe functioned through the melting phase transition of Hg (-38.8^o C)